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Review Article

HYBRID BIOGENIC ADSORBENTS TO REMOVE HEAVY METALS FROM WASTE WATER: CAN IT BE A SUSTAINABLE GREEN PROTOCOL TO MINIMISE ENVIRONMENTAL AND OCCUPATIONAL HAZARDS ?

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ABSTRACT

Presence of heavy metals in waste water cause biological imbalance and environmental hazards. Various conventional and aggressive chemical protocols were employed for effective removal of heavy metals from waste water. Certain disadvantages like unwanted toxic by-products, high cost, environmental and occupational hazards pave the way for using of biogenic and hybrid adsorbents. Various active organic functional groups and larger adapted surface area in biogenic and hybrid adsorbents enhance the adsorption competence remarkably. Enhanced adsorption capacity depends on appropriate preparation techniques, variation of initial metal concentration and contact time etc. We will emphasize effectiveness of using hybrid biogenic adsorbents rather than general biogenic materials.

Keywords: Waste water, Environmental and occupational hazards, adsorption competence, hybrid adsorbents, biogenic material.

1. INTRODUCTION

Water, the most essential component in ecosystem and human living organism, is polluted immensely by water pollution, industrial effluents, heavy metals and pesticides [1]. Various physio-chemical parameters are the indications of potable and usable water.

Sustainability with green approach is need of the hour for smooth manoeuvrings of pollution free environment as well as maintenance of healthy ecosystems. Random industrialisation without proper obeyance of standard protocols leads to improper handling of effluents containing large number of toxic heavy metals which primarily origins pollution of water results into environmental and occupational health hazards. Orthodox processes such as reverse osmosis, Ultra-filtration etc are inept of quantitative assessments and efficient removal of heavy metal in low concentration from industrial effluents. Humans are greatly affected by various irreversible diseases caused by heavy metals viz., Hg, Cd, Cr, Pd, Co, As, Pb, Zn etc. Conventional chemical methods with aggressive protocols due to their indirect destructive impact on environment and high cost are not best appropriate techniques for effective removal of heavy metals from waste water. Adsorption process by natural adsorbents is one of the best alternatives to remove toxic heavy metals from industrial waste water. Effective implementation of adsorption capacity by chicken feather, hair, natural seeds and plants, daily wastages stuffs etc have been reported so far. Low concentration of heavy metals in waste water can also be efficiently removed by biogenic adsorbents. Kinetics of adsorptions is also evident from various kinetic studies such as Freundlich and Langmuir Adsorption isotherm. Certain active bio molecules or inorganic mixed oxides can be functionalised with biogenic materials for enhancement in adsorption capacity. Functionalised molecules can be recovered easily from the treated water due to minimum solubility and recyclable protocols. Morphological analysis such as FTIR, SEM, TEM etc reveals their effective structural advantages and contact time, pH, and initial concentration dependent adsorption parameters supports effectiveness as hybrid adsorbent to remove toxic heavy metals from waste water. Classifications of nano-based water treatment are mentioned in various literatures [12-14].

Table 1: Standard permissible limits in waste water (effluents) and adverse health effects caused by specific toxic heavy metals

Toxic heavy metals (Pollutants)	Major available sources	Adverse health effects	Standard permissible limits in waste water (effluents) in ppm by various organization		References
Hg	Hydroelectric, mining, pulp, paper industries. coal burning, incineration and Chloro-alkali industry	Tremors; Emotional changes	WHO	0.001	[2,3]
			China	0.005	
			USEPA	0.00003	
			World Bank	0.01	
			India CPCB	0.01	
Cd	Smelters, marble, steel, and metal plating industries.	Flu-like symptoms, damage lungs.	WHO	0.003	[4,5]
			China	0.03	
			USEPA	0.01	
			World Bank	0.1	
			India CPCB	1.0	
Pb	metallurgical, chemical and petrochemical industries	Anemia, weakness, kidney, brain damage,	WHO	0.01	[6,7]
			China	1.0	
			USEPA	0.006	
			World Bank	0.1	
			India CPCB	1.0	
Cr (Hexavalent)	Discharges from steel and pulp mills, and erosion of natural deposits of chromium-3.	Targets the respiratory system, kidneys, liver, skin and eyes, cancer	WHO	0.05	[8,9]
			China	0.5	
			USEPA	0.05	
			World Bank	0.5	
			India CPCB	2.0	
Ni	Sludge, and in slags and fly ashes from waste incineratos, phosphate pesticides	Allergy, cardiovascular and kidney diseases, lung fibrosis, lung and nasal cancer	WHO	0.02	[10,11]
			China	1.0	

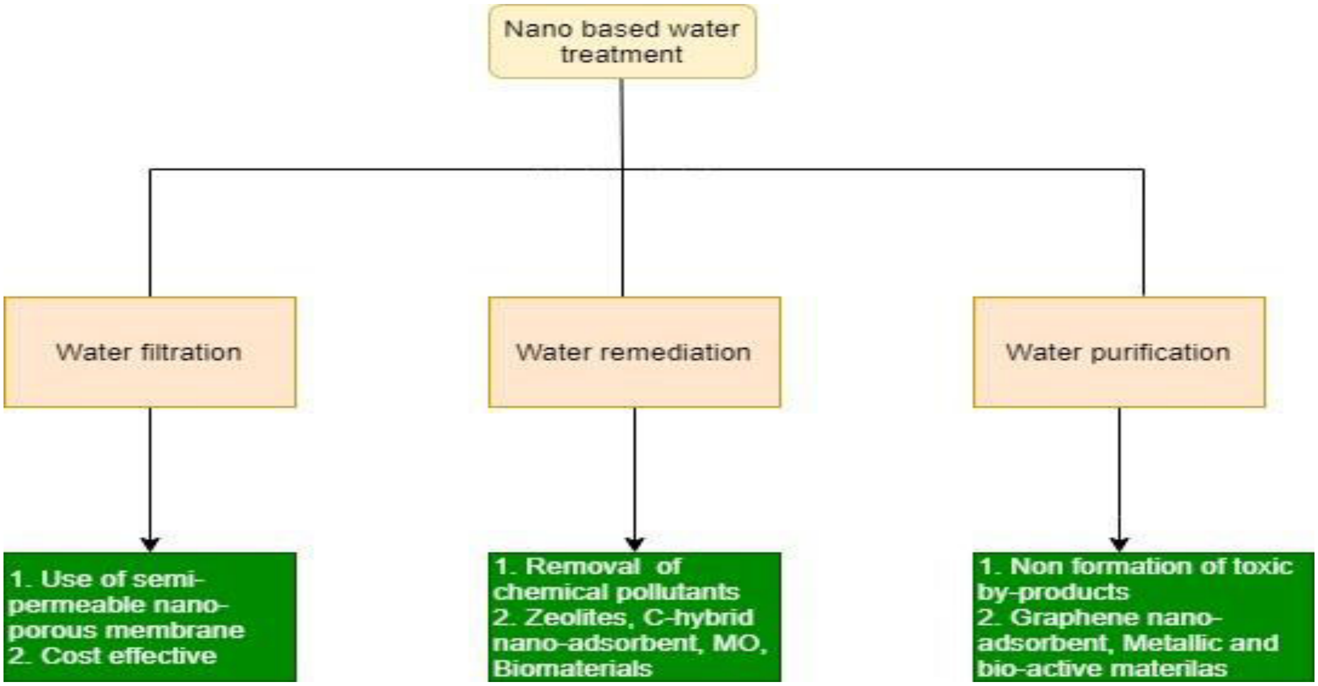

Fig. 1: Schematic classification of nano-based water treatment

2. USE OF NANO MATERIALS IN WASTE WATER TREATMENT

Carbon based nano materials (CBNs) are derived from activated granular carbon and due to its versatile mechanical strength and biocompatibility; it is treated as efficient adsorbent for removal of heavy metal ions from polluted water. It has certain disadvantages viz., slow kinetics and regeneration in aquous medium [15]. To ward off the disadvantages, use of new generation hybrid carbon nano materials such as CNTs, functionalised graphene oxides, biogenic nano materials /nanocomposites have been alternatively used [16].

2.1. Classification of Carbon Nano-materials on the basis of relative dimensions [17-19]

I. Zero-dimensional (0-D) nanomaterial (all dimensions <100 nm) e.g., fullerene and quantum dots
II. One-dimensional (1-D) nanomaterials (two dimensions <100 nm, one dimension >100 nm) e.g., carbon nanotubes
III. Two-dimensional (2-D) nanomaterials (two dimensions >100 nm) e.g., graphene.
IV. Three-dimensional (3-D) materials (all dimensions >100 nm) e.g., graphite and nanocomposites.

2.2. Application of Graphene oxide in waste water treatment

Graphene is stable in water due to the existence of extensive H-bonding throughout graphene layer. Proper pore size in Graphene oxide and considerable formation of thin films, waste water can be treated efficiently due to the encapsulation of metal ions inside the thin layer moiety. Graphene oxide, by the virtue of strong hydrophilic character, can act as desalinating agent and water can flow with minimum hindrance between grapheme oxide membranes [20-22]. Graphene based materials can be used as biocompatible nano-porous materials to remove heavy metals from polluted water [23-26]. Table 2 illustrates the advantages of various microstructures in Graphene oxide (GO) for the enhancement of sorption efficiency.

Table 2: Efficacy of engineered GO in removal of dissolved metal ions from polluted water

Metal ions	Hybrid Modified graphene oxide	Sorption capacity in (mg/g)/removalefficacy in %	References
As^{3+}	Porous graphene materials	80%	[27]
Pb^{2+}	Reduced graphene oxide+ Fe_3O_4	373.14 mg/g	[28]
Pb^{2+},Cu^{2+}, Ni^{2+}, Cd^{2+}, and Cr^{3+}	Reduced graphene oxide with 4-sulfophenylazo (rGOs)	689, 59, 66, 267 and 191mg/g respectively	[29]
Pb^{2+}	Graphene-based self-propelled microbot system	80%	[30]
Mn^{2+}	Hydrogen beads using graphene oxide and sodium alginate (GO-SA)	56.49mg/g	[31]
Pb^{2+}	Zinc oxide with tea polyphenol with reduced graphene oxide (TPG-ZnO).	98.9%	[32]
Pb^{2+}	GO+ Fe_3O_4	98% removal efficiency and sorption capacity of 126.6 mg/g	[33]
Pb^{2+}	Graphene-hydrogel lingo sulfonate functionalized Nanocomposites	1308 mg/g	[34]
Hg^{2+}	Graphene oxide with chloroacetic acid (GO-COOH) and ethylenediamine (GO-amino).	122 mg/g and 230 mg/g respectively	[35]
Fe^{2+}, Mn^{2+}	Magnet graphene oxide	-	[36]
Cu (II), Pb (II), Fe (II), and Mn (II)	Graphene-based adsorbent	-	[37]
Pb^{2+}	GO+Al_2O_3	96% removal efficiency	[38]
Mn^{2+}	Reduced GO+ Fe_2O_3	425 mg/g	[39]
Cr^{6+}	Membrane GO	372 mg/g	[40]

2.3. Application of carbon nano-tube (CNT) in waste water treatment

Carbon nanotubes are classified depending on relative surface area (150-1500 m^2/g) and continuing of graphene sheets as follows [41]:

- Single-wall (SWCNTs), approximate diameter between 0 and 3 nm; e.g., layered rolled up grapheme
- Multiwall carbon nanotubes (MWCNTs), extent to 100 nm of diameter e.g., multilayered rolled up graphene

CNT can be used in diode junction and efficiency of photovoltaic cell is enhanced to multiple extents. Meso pores in CNT and its photo catalytic activity makes its viable to remove heavy metals from polluted water [42]. Leiva et al. [43] showed the implications of dispersion effect on the exercise of CNTs for the removal of heavy metals. Hydrophobic character of CNT and specific toxicity on certain aquatic organisms are the noteworthy disadvantages of using CNT. Application through column membrane technology and derivativesation with organic functional groups results in suitable use of CNT in waste water treatment [44]. Various operational factors such as contact time, optimum pH play an important role for the enhancement of adsorption capacity/efficiency using CNT as an adsorbent [45].

Table 3: Illustration of various factors on the adsorption capacity of CNT based adsorbents for the removal of heavy metal ions

Metal ions	CNT based adsorbent	Contact time in hrs	optimum pH	Adsorption capacity (mg/g)/efficiency (%)	Reference
Hg^{2+}	SWCNTs	1.50	7.94	41.66 mg/g	[46]
Hg^{2+}	SWCNTs-Fe_3O_4-CoS	0.11	5.26	1666 mg/g	[46]
Cr^{6+}	SWCNTs-polysulphone (membrane)	Flux through membrane	2.6	96.8%	[47]
As^{3+}			-	87.6%	
Pb^{2+}			-	94.2%	
Cr^{6+}	SWCNTs	1.00	2.5	2.35mg/g	[48]
Cr^{6+}	MWCNTs	1.00	2.5	1.26mg/g	[48]
Cr^{3+}	Functionalized MWCNTs	3.00	6.0	99.83%	[49]
Pb^{2+}	Al_2O_3-MWCNTs	1.00	7.0	90%	[50]

2.4. Application of fullerene in waste water treatment

Fullerene is represented by the general formula C_{20+m} (m= integer). Fullerene has minimum accumulation tendency and larger surface area. Due to these two exceptional morphological characteristics, heavy metals can be adsorbed in between the voids and defects of nanosheets of fullerene [51]. High mobility and enhanced hydrophobic character of fullerene in comparison to other polymeric nano-composites such as poly-styrene remarkably enhance its removal capacity of Cu^{2+}. Kinetic study of the potential removal of Cu^{2+} is also supported by Langmuir adsorption isotherm. Surface area can be altered when fullerene is structurally embedded with zeolites, lignin or other compatible polymeric materials. Fullerene is found to be used in membrane technology due to its various thermophysical properties such as tiny structures with large surface area, friendly recyclability, and easy mode of fictionalization etc. Polymeric grafting of fullerene with poly vinyl pyrrolidone produces antibacterial material which is used as water disinfectant [52].

2.5. Application of biogenic nanoparticles in waste water treatment

Plant extracts, leaf, yeast, fungi etc. are the precursors to prepare biogenic nanomaterials. Generally, biologically active natural molecules are combined with specific metal salts and under non-destructive conditions NP is obtained. Impurity removal from the biogenic NP is the major challenge. Significant advantages of biogenic NPs are cost effectiveness, easily available precursors and non-invasiveness [53]. Synthesized NPs can be strategically combined with other bioactive molecules for the potential enhancement of surface area and activity.

2.6. Application of nano photo catalysts in waste water treatment

Nano photocatalyst in presence of light can biodegrade organic pollutants as well as reduce dissolved metal ions [68]. Ag (I) can be removed with removal efficiency of 99.7% by P25 TiO_2. Photocatalytic reduction depends on redox potentials. It has been experimentally observed that if $E°_{1/2}$ of metals > 0.3 eV, dissolved metal ions can be reduced to its removable form of corresponding metal and deposit on larger surface.

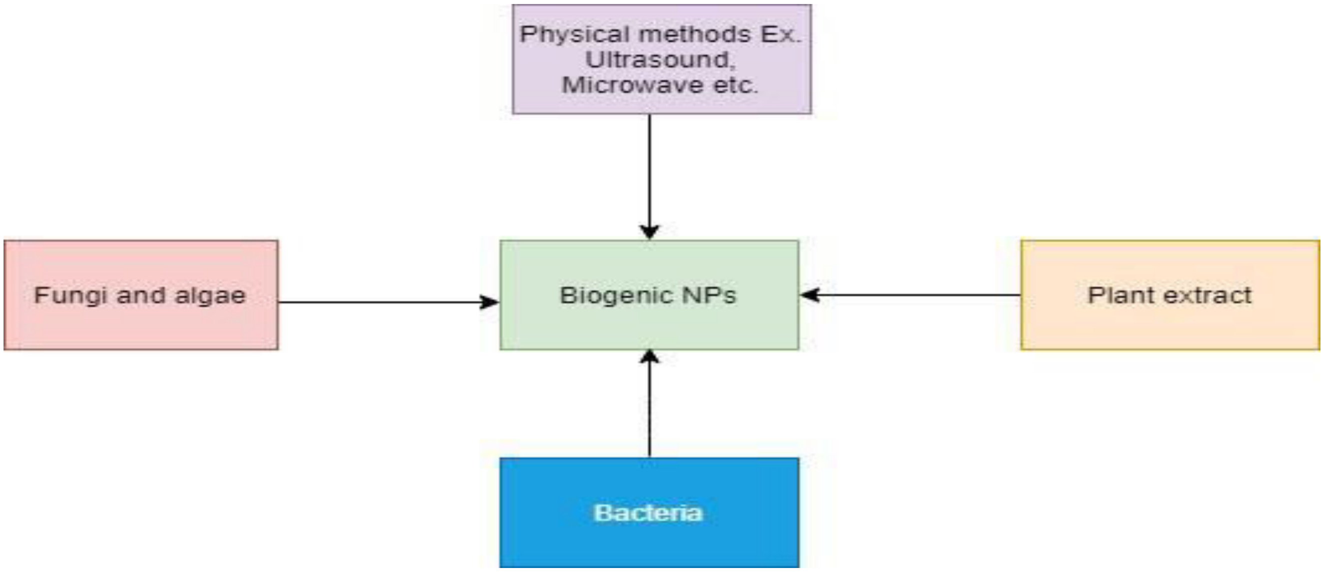

Fig. 2: Schematic representation of various precursors for the synthesis of Biogenic NPs

Table 4: Maximum adsorption capacities of biogenic NPs for the removal of heavy metal ions

Metal ions	Biogenic NPs	Maximum adsorption capacity	References
As (III)	Fe_2O_3 NPs using Aloe vera leaf extract	38.47 mg g^{-1} at 20°C.	[54]
As(III) As (V)	magnetic iron oxide NPs from tea waste	88.69 mg g^{-1} 153.8 mg g^{-1}	[55]
As (III)	iron oxide NPs usingeucalyptus extract+ Chitosan	147 mg g^{-1}	[56]
As (III) As (V)	Iron oxide NPs using*M. ferrooxydanson*	104.53 mg g^{-1} 48.06 mg g^{-1}	[57]
Cr (VI)	Modified Fe NPs using *P. granatum* extract + yeast *Y. lipolytica* (NCIM3589/NCIM 3590)	125.0 and 156.3 mg g^{-1} (NCIM 3589/NCIM 3590)	[58]
Cr (VI)	Fe NP using *Eucalyptus globules* leaf extract.	98.1%	[59]
Cr (VI)	Fe NPs by using different plant and fruit extracts (*Camellia sinensis, Syzygiumaromaticum, Mentha spicata and Punica granatum*)	500 mg g^{-1}	[60]
Cr (VI)	Fe NPs synthesized by *S. jambos*	698.6 mg g^{-1}	[61]
Cr (III) and Pb (II)	Fe NP using CLC	105.6 and 102.3 mg g^{-1} respectively	[62]
Cd (II)	CdS NP using *P. aeruginosa*	88.66% removal of Cd, 48 h contact time	[63]
Cd (II)	Fe NPs synthesized from tangerine peel extract	91% removal of Cd	[64]
Zn (II)	Se NPs using anaerobic granular sludge	70%	[65]
Cu (II)	Fe NPs using *S. thermolineatus*	85%	[66]
Hg	Se NPs from bacterial EPS	81.2%	[67]

Table 5: Photo catalytic action of TiO_2 on the efficient removal of specific metal ions

Metals ions to be removed/ aggregation on the TiO_2 surface, 0.1 wt% of TiO_2	Efficient removal	References
Ag(I)	Yes	[69, 70]
Au (III)	Yes	
Cr (VI)	Yes	
Hg (II)	Yes	
Pb (II)	Yes	
Mn (II)	Yes	
Pt (IV)	Yes	
Cd (II)	No	
Ni (II)	No	
Fe (II)	No	

3. CONCLUSIONS AND FUTURE PERSPECTIVES

Environmental and occupational health hazards affect biological and chemical environments such as contamination of water through agricultural and industrial contamination of water and land. Uncontrolled use of pesticides and organic contaminants produces reactive oxygen species (ROS) which induces DNA methylation and genetic disorders. Hence, identification and efficient removal of dissolved heavy metals in polluted water are the need of the hour. Use of fabricated hybrid nano-catalyst having larger surface area, wide nanosheets and regenerative properties are the sustainable routes to prevent adverse health hazards. Our report on the applications of various hybrid nanomaterials clearly showcases the enhancement of adsorption efficacy and strict adherence of green synthesis protocols.

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Conflict of interest

Authors declare that they have no conflict of interest.

5. REFERENCES

1. Muhammad S, Risky K, Adhi Y, Tony H, Jongtae R, Wedad AA, Tahani S, *Int J Environ Res Public Health*, 2021; **18:**468.
2. Onuegbu TU, Umoh ET, Onwuekwe LT, *Int J Sci and Tech,* 2013; **2:**169-173.
3. World Bank. Project guidelines: Industry sector guidelines. Pollution Prevention and abatement Handbook, 1998.
4. Sahmoun AE, Case LD, Jackson SA, Schwartz GG, *Cancer Invest*, 2005; **23:**256-263.
5. Hutton M, *Eco and Env Safety*, 1983; **7:**9-24.
6. Babel S, Kurniawan TA, *J Haz Mat*, 2003; **97:** 219-243.
7. Jacques G, James AJ, Cynthia PA, Chromium (VI) Handbook.1st ed. CRC Press; 2004.
8. Ray RR, *Interdisciplinary Toxicology,* 2016; **9:**55–65.
9. Sun H, Brocato J, Costa M, *Curr Envir Health Rpt,* 2015; **2:**295-303.
10. Genchi G, Carocci A, Lauria G, Sinicropi MS, Catalano A. *Int J Env Res Pub Hea*, 2020; **17:**679.
11. Das KK, Das SN, Dhundasi SA, *The Ind J Med Res,* 2008; **128:**412-425.
12. Mohmood I, Lopes CB, Lopes I, Ahmad I, Duarte E, Armando CP, *Env Sci Poll Res,* 2013*;* **20:** 1239-1260.
13. Santhosh C, Velmurugan V, Jacob G, Jeong SK, Grace AN, Bhatnagar A, *Chem Eng J,* 2016; **306:** 1116-1137.
14. Cincinelli T, Alessandra Martellini E, Coppini DF, Katsoyiannis A, J. *Nanosci Nanotech,* 2015; **15:** 3333-3347.
15. Adeleye AS, Conway JR, Garner K, Y. Huang, Y. Su, *Chem Eng J,* 2016; **286:**640-662.
16. Uzma H, Hilal A, Khalid U, Tabassum P, Micro and Nano Technologies, Chapter 11, Elsevier, 2019.
17. Han X, *Inter J Oleo Sci,* 2016; **65:**1-7.
18. Lee K, Mazare A, Schmuki P, *Chem Rev,* 2014; **114:**9385-9454.
19. Singh RP, *Int J Electrochem,* 2011; **2011:**1-30.
20. Saifullah B, *Molecules*, 2017; **22:**1560.
21. Elsehly E, *Water Supply*, 2015; **16(2):**347-353.
22. Rahman MM, Sime SA, Hossain MA, Shammi M, Uddin MK, Sikder MT, et al. *Arab J Sci Eng*, 2017; **42:**261-269.
23. Aifullah B, *Nanomaterials*, 2018; **8(10):**820.
24. Dorniani D, *Nanoscale Res Lett*, 2016;**11(1):**491,1-9.

25. Ray SC, William Andrew Publishing, Oxford, 2015, 1-38.
26. Ray SC, Editor, William Andrew Publishing: Oxford, 2015, 39-55.
27. Tabish TA, *Sci Rep*, 2018; **8(1):**1817.
28. Guo T, *Adsorption Sci Technol,* 2018; **36(3-4):**1031-1048.
29. Jhang CZ, *Sep Sci Technol*, 2018; **53(18):**2896-2905.
30. Vilela D, *Nano Lett*, 2016; **16(4):**2860-2866.
31. Yang X, *Sci Rep*, 2018; **8(1):**10717-10717.
32. Zheng S, *J Biomed Nanotechnol,* 2018; **14(7):**1263-1276.
33. Mousavi SM, *Phys Chem Res*, 2018; **6(4):**759-771.
34. Thakur S, *Vacuum,* 2017; **146:**342-355.
35. Zhang CZ, Chen B, Bai Y, Xie J, *Sep Sci Technol*, 2018; **53(18):**2896-2905.
36. Yan H, *Appl Mater Interfaces*, 2014; **6(12):**9871-9880.
37. Ali I, *Environ Int,* 2019; **127:**160-180.
38. Aguilar-Pérez KM, Avilés-Castrillo JI, Ruiz-Pulido G, *Case Stud Chem and Envi Eng*, 2020; **100028:**1-5.
39. Morsi RE, Alsabagh AM, Nasr SA, Zaki MM, *Int. J. Biol. Macromol,* 2017; **97:**264-269.
40. Thines RK, Mubarak NM, Nizamuddin S, Sahu JN, Abdullah EC, Ganesan P, *J Taiwan Inst Chem Eng*, 2017; **72:**116-133.
41. Vidu R, *Front Syst Neurosci*, 2014; **8(91):**1-24.
42. Yamada K, *PLoS One*, 2014; **9(9):**105767.
43. Rodríguez C, Briano S, Leiva E, *Molecules*, 2020; **25(14):**3106.
44. Rahman MM, Sime SA, Hossain MA, *Arab J Sci Eng,* 2017; **42:**261-269.
45. Raphey VR, *Mater Sci Eng C*, 2019; **100:**616-630.
46. Burakov AE, *Ecotoxicol Environ Saf*, 2018; **148:** 702-712.
47. Mauter MS, Elimelech M, *Environ Sci Technol*, 2008; **42(16)**:5843–5859.
48. Gupta RK, *J Mater Chem A*, 2017; **5(31):**16025-16058.
49. Andrews R, *Acc Chem Res*, 2002; **35(12):**1008-1017.
50. Thang HB, Quang LD, Hong NM, Phan Hong Khoi, Minh PN, *J Nanomat*, 2014; 1-6.
51. Chae SR, Hotze EM, Wiesner MR, Chapter 21 - Possible Applications of Fullerene Nanomaterials in Water Treatment and Reuse, In Micro and Nano Technologies, Nanotechnology Applications for Clean Water (Second Edition), William Andrew Publishing, 2014.
52. Pulicharla R, Zolfaghari M, Brar SK, Cledon M, Drogui P, Surampalli RY, *J Haz Toxic Radioact Waste*, 2016; **20 (1):** 1-12.
53. Gautam PK, Singh A, Misra K, Sahoo AK, Samanta SK, *J Env Management*, 2019; **231:** 734-748.
54. Mukherjee D, Ghosh S, Majumdar S, Annapurna K, *J Environ Chem Eng,* 2016; **4:** 639-650.
55. Lunge S, Singh S, Sinha A, *J Magn Magn Mater*, 2014; **356:** 21-31.
56. Cabanas M, López-García M, Barriada M, Herrero JL, Vicente R, *Chem Eng* J, 2016; **301:** 83-91.
57. Andjelkovic I, Azari S, Erkelens M, Forward P, Lambert MF, Losic D, *RSC Adv,* 2017; **7:** 3941-3948.
58. Rao A, Bankar A, Kumar AR, Gosavi S, Zinjarde S, *J Contam Hydrol*, 2013; **146:** 63-73.
59. Madhavi V, Prasad T, Reddy AVB, Reddy BR, Madhavi G, *Acta A Mol Biomol Spectrosc*, 2013; **116:** 17-25.
60. Mystrioti C, Xanthopoulou T, Tsakiridis P, Papassiopi N, Xenidis A, *Sci. Total Environ*, 2016; **539:** 105–113.
61. Xiao Z, Yuan M, Yang B, Liu Z, Huang J, Sun D, *Chemosphere*, 2016; **150:** 357-364.
62. Lingamdinne LP, Chang YY, Yang JK, Singh J, Choi EH, Shiratani M, et al. *Chem Eng J,* 2017; **307:** 74-84.
63. Rai M, Yadav A, Gade A, *Crit. Rev. Biotechnol,* 2008; **28:** 277-284.
64. Ehrampoush MH, Miria M, Salmani MH, Mahvi AH, *J Environ Health Sci Eng*, 2015; **13:84**.
65. Jain R, Jordan N, Schild D, Hullebusch V, Weiss ED, Franzen S, et al. *Chem Eng J,* 2015; **260:** 855-863.
66. Kandasamy R, *Separ Purif Technol*, 2017; **188:** 458-467.
67. Wang X, Zhang D, Qian H, Liang Y, Pan X, Gadd GM, *Sci. Total Environ*, 2018; **613:** 672-678.
68. K.P. Mehta, R. Sharma, S. Haldar et al., Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2021.07.253 (Article in press).
69. Prairie MR, Evans LR, Stange BM, Martinez SL, *Environ Sci Tech*, 1993; **27(9):** 1776-1782.
70. Fu H, Lu G, Li S, *J Photochem and Photobio A: Chemistry*, 1998; **114(1):** 81-88.